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PATTERSON FUNCTIONS AND VECTOR SETS*

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PATTERSON'S FUNCTION, WHAT, WHY, AND WHY NOT?

In this era of automation, it is but natural that crystallographers think about the possibility of letting a high speed digital computer automatically solve the structure of a crystal from the experimentally measured x-ray intensity data. Starting with the data, two paths are clearly open. The first one involves the direct use of intensities in the formalism of Karle, Hauptman and others. The second, but certainly the earlier approach, is that of Patterson and his function.

In this approach we take the Fourier transform of the data, and work with it in the formalism of Buerger[1] and others[2,3,4,5]. Here it is not out of place to ask which procedure is to be preferred. But such a question carries an implication that there is something quite drastically and characteristically different about the two procedures. It appears to us, speaking in broad terms, that this is not really so. After all, we all start with the intensities, and most probably, we are not going to get any more information out of the data than what is actually present, by merely changing the mathematical formulation. Clearly, what is proven to be useful is the introduction of auxiliary information of a physical and chemical nature. Here, we feel that the introduction of such auxiliary criteria is more easily accomplished with Patterson's function, though conceivably the same thing could be done with the direct methods. When all is said and done, the former certainly avoids undue and unwarranted mathematics, and comes within the domain of elegant and practicable programming. That is the main reason why our vote has been for Patterson's function. Of course, the proof of the pudding is in the eating, and the choice of a particular approach may well be more a matter of taste than anything else.

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THE CENTRAL PRINCIPLE

The principle underlying all variants of Patterson's method is the plain, simple fact that information about the crystal structure is contained by the intensity data in the form of the peaks of the interatomic vectors. These peaks are the peaks of Patterson's function, which is simply a Fourier series involving the x-ray intensity data, $F(\vec{H})^2$, as the Fourier coefficients, i.e.,

$$P(\vec{u}) = \frac{1}{V} \sum_{\vec{H}} |F(\vec{H})|^2 \exp + 2\, i\, \vec{H} \cdot \vec{r}$$

In principle, the synthesized function is supposed to contain peaks at the N^2 interatomic vectors $\vec{r}_i - \vec{r}_j$ (i, j = 1, N, the total number of atoms per unit cell). But in practice, they do not always contain all the peaks, more so if one adopts procedures of sharpening.

THE PROS AND CONS OF SHARPENING

By now, it is well known that given a vector set, that is, given the N^2 interatomic vectors, it is possible to obtain the structure in quite a straightforward way.

It is equally well known that Patterson functions are very poor approximations of the corresponding vector setup, because the functions have considerable overlapping of peaks, unless the crystal structure under investigation is far too simple. For that reason, procedures of peak sharpening have been developed. However, commonly available sharpening procedures appear to take the intensity data, correct or even over correct them for thermal vibrations, in the approximation of the Debye-Waller factor, and then modify them into such quantities as unitary intensities, normalized intensities, etc., and use them as the coefficients in the calculation of a sharpened Patterson function. No doubt, the sharpened coefficients correspond to the intensities given by a structure of non-vibrating and point atoms. But the mere use of a limited number of point atom intensities in the Fourier summation does not give back a point atom Patterson for the simple reason that the intensity distribution is one which is abruptly truncated in reciprocal space. As a result, the peaks still have widths. Secondly, some of the Patterson peaks get washed out by the negative ripples which are inevitable in these sharpening procedures. These two facts cause lots of troubles, particularly in the case of equal atom structures of moderate complexity. For this reason, it is not surprising that Martin Buerger[6] has gone to the extent of teaching, and we quote, the moral, "Don't sharpen your Patterson function and then wonder why your use of the minimum function did not lead to a successful conclusion." But it is equally true that if one looks at the unsharpened Patterson function of a crystal of moderate complexity, then it is very difficult to get a good starting point for carrying out subsequent image-seeking procedures. Therefore, it is certainly useful to develop two methods. First, we have got to extend the range of the Patterson coefficients. Second, we have got to retrieve and supply any information, either already missing in the unsharpened function, owing to experimental errors, or more often than not, any information unfortunately lost, because of the use of point atom intensities.

EXTENSION OF THE RANGE OF THE COEFFICIENTS BY THE METHOD OF FOURIER INVERSION[7,8,9]

The question of extension of the range of the coefficients is open. Here, we believe we can do something. First of all, it is useful

THE DEVELOPMENT OF THE VECTOR SET OUT OF THE PATTERSON FUNCTION

Now arises the very tempting possibility of combining the iterative procedure of Fourier inversion with that of the 1MA($\vec{u}$), and attempt to develop the vector set, out of the Patterson function. Is this procedure possible? The answer clearly depends on the structure. In this context it is useful to classify structures as rational and irrational. A rational structure has atomic coordinates which are expressible as rational members. They have the important property that the point atom intensity distribution is triply periodic in reciprocal space, so that it is possible to define a supercell. If each reciprocal lattice point is weighted by the corresponding value of the point atom intensity, then the vector set is obtained from a Patterson function synthesized with all the coefficients contained within one supercell. In other words, knowing the coefficients within part of the supercell, one develops the remaining coefficients by the iterative technique of Fourier inversion and finally obtains the vector set. As to irrational structures, the answer is not so clear cut. Here the question is what is the multiplicity of the supercell which is meaningful and consistent with the accuracy of the experimental data? To date, we do not have a precise answer for this. However, a preliminary idea regarding the multiplicity of the supercell relevant to a given case may be inferred by calculating the value of the coefficient of indices (0, 0, 0), and those of indices which are multiples of 10 by the technique of Fourier inversion. The multiplicity of the supercell is approximately the same as the indices whose coefficient has a value close to that of the origin term. In any case, rational structure or irrational structure, the use of the Fourier inversion technique and the 1MA function yields much sharper peaks along with the retrieval of the missing peaks.

THE GENERALIZED IMPLICATION FUNCTION

Having obtained a good starting point, namely a sharp Patterson function, how does one go about determining the structure? A very useful information, in this context, is certainly the apriori knowledge of the space group symmetry of the crystal. The basic idea of exploiting the crystal space symmetry in the interpretation of the Patterson function has been given to us by Martin Buerger in his formulation of the implication theory. We, as well as other workers, have generalized his ideas into higher orders and higher dimensions, though certainly the generalization is implicit in Buerger's work.

The central idea of this kind of approach is simply stated as follows: If the space group symmetry is completely or even partially known, then one knows even at the very outset, a certain number, say n, of equivalent points. One can then store an asymmetric unit of the Patterson function in the computer, and calculate therefrom the zero order function. The essential idea is as

to employ shorter x-ray wavelengths, and collect data at lower temperatures. In most cases, this procedure may be highly desirable but not absolutely essential for one to undertake analytical methods of extending the range of the coefficients. One such analytical method is as follows.

One synthesizes the sharpened Patterson function with the available data, and then resorts to an iterative procedure of coefficient extension and information retrieval. Each iterative cycle involves three steps.

Step 1 - involves the coefficient synthesis. This synthesis is calculated by the Fourier inversion of Patterson's synthesis, and is given by

$$I_s(\vec{H}) = k \sum_{\vec{r}} P_m(\vec{r}) \exp -2\pi i \vec{H} \cdot \vec{r}$$

Here, the Fourier coefficients are the values $P_m(\vec{r})$ of the Patterson function which has been modified by replacing all values of $P(\vec{r})$ P_{min}, the expected peak height for an interatomic vector, by zeros. This is one method by which the concept of a point atom, so central in the development of a vector set, is introduced into the computing process. Second, any available stereochemical information may be introduced to great advantage. At the very least, one can make the function value = 0 at all points, except the origin, within a sphere of radium d_{min} constructed around the origin peak. This procedure takes care of the requirement that no two atoms can approach each other by a distance less than d_{min}.

Step 2 - consists in checking the new coefficients, and making negative ones zero. This procedure is equivalent to introducing the concept of the non-negativity of the intensity distribution.

Step 3 - consists in synthesizing a new $P(\vec{r})$ in which the coefficients are those of the starting set plus the additional ones. The iterations proceed, and in each cycle the range is extended in steps of small increments.

THE QUESTION OF RETRIEVAL OF THE MISSING INFORMATION

It is highly desirable that we supply the computer a good starting point, namely a very sharp Patterson function which has all the required peaks. Now, how do we retrieve any information which has been lost? The answer may be given by remembering that even though a given peak, say the one at $\vec{r}_c - \vec{r}_d$, is missing, the Patterson function still contains information about this peak in the very many peaks at $\pm (\underline{r}_c - \underline{r}_j)$ and $\pm (\underline{r}_d - \underline{r}_j)$ where subscripts c and d refer to specific atoms, and j is a running subscript. So that all the computer has to do is to collect this information and present it at the location of the missing peak. This operation is done quite conveniently by the accumulation of minimum function, in the first order stage.

$$\text{MA}(\vec{u}) = k' \sum_{\vec{r}} \text{Min} \{P(\vec{r}), P(\vec{r} + \vec{u})\}$$

follows: The computer asks the question, is there an atom at a given grid point (I, J, K)? To find the answer, the computer works out the grid points which are symmetry equivalent to (I, J, K), and then compares the interatomic vectors among these n grid points. Then it looks up the values of the Patterson function at these $(n^2 - n)/2$ points, and if the values are compatible, then there is an implication that we have an atom at (I, J, K). The computer can carry out any one of a number of operations on the Patterson function values at the $(n^2 - n)/2$ points, and arrive at a suitable measure for the implication of an atom at the grid point (I, J, K). The various operations can be (1) summation, (2) multiplication, and (3) extraction of the minimum of the Patterson function values.

In the calculation of lower order functions, including the zero order, the operation of the extraction of the minimum is probably the best. But this operation may become quite drastic at higher orders. In such cases, it is probably useful to take the sum of the last few minima. Alternatively, one may accept a certain level P_{min} for the expected peak height of an interatomic vector, and count how many times the actual value exceeds P_{min}, as the computer searches the $(n^2 - n)/2$ points, and assign this count as the measure of the implication of an atom at (I, J, K).

The calculation is to be repeated for all grid points in one asymmetric unit of the crystal space, and the output is the zero order function. It is well known that the symmetry of the zero order function is much higher than that of the space group, and for this reason, the zero order function, by itself, often fails to determine the complete structure. But the purpose of the calculation is only to provide one or more possible atomic positions, located with respect to the origin of the space group. In all cases, any one peak may be chosen as the position of one atom, so long as this peak is not spurious.

One can then go into a calculation of the first order function. At this stage, one uses as input, not only the space group symmetry, but also the positional coordinates (I_1, J_1, K_1) of one atom, as determined from the zero order calculation. The calculation at a typical grid point (I, J, K) involves looking at the Patterson function values at the cross vectors between the grid point (I, J, K) and the atom at (I_1, J_1, K_1) and its symmetry equivalents.

The iterations proceed to higher orders in a similar fashion, so that in the p^{th} order stage, one uses as input the positions of p atoms. At each stage one increases the number of input atoms. The positions of the additional input atoms are derived from preceding calculations. As the iterations proceed to higher orders, the extra symmetry of the zero order function vanishes. One may continue the iterations until sufficient number of atoms (usually 50% of the total) can be discovered, enabling one to calculate the Fourier. In some cases, the iterations may proceed to complete the entire structure determination.

SOME RESULTS

The correctness of most of the above ideas has been verified by detailed calculations on simulated equal atom structures. As to actual crystals, the formalism of the generalized implication functions was systematically used by Dr. F. B. Gerhard[10] of our laboratory to solve the structure of the mineral pachnolite: This crystal is monoclinic, a = 9.915A, b = 10.432A, c = 15.716A, and β = 142.26; 8 molecules per cell, each molecule of formula $NaCaAlF_6 \cdot H_2O$; space group strictly A_2, though A_2/a is closely approximated. The significance of this work is that not only that the computer which was used was comparatively a small machine, namely IBM 1620 - Model II, but also the fact that there were ambiguities regarding the space group itself. An interesting anecdote is that the first atom which was discovered from the zero order function and used as the starting point for subsequent iterations turned out to be aluminum, and interestingly enough, the calcium atom, the heaviest one in the structure, was discovered only in the later iterations from considerations of peak heights.

ACCUMULATION FUNCTIONS, AND THE FUTURE

The next major step in the interpretation of Patterson's function may well be the replacement of the presently available image seeking functions by the accumulation functions.[11,12] These are integrals of the corresponding image seeking functions. The most promising ones appear to be the accumulation of minimum functions. In the p^{th} order stage, this function is given by

$$pMA(\vec{u}) = \sum_{\vec{r}} \text{Min } \{P(\vec{r}),\ P(\vec{r}+\vec{u}_1),\ \ldots,\ P(\vec{r}+\vec{u}_p),\ P(\vec{r}+\vec{u})\}$$

Here, Min is the operation of extracting the minimum among the Patterson function values within the parenthesis. The summation is over one unit cell. $(\vec{u}_1, \vec{u}_2, \ldots, \vec{u}_p)$ are a set of interatomic vectors, defining a fragment of a given image. When such a fragment is known, then the calculated $pMA(\vec{u})$ contains peaks at all the atoms of the entire image. Certain properties are characteristic of the $pMA(\vec{u})$ function. First, the peak heights at the unknown atoms are more or less the same as those at the atoms which were used as input. Second, the effect of including an incorrectly placed atom in the input is so drastic that in some cases even the input atoms, which the investigator knows for certain to be correct, do not show up in the output. This drastic effect takes place only if position of the input atom is completely incorrect. However, if the input atoms are correctly placed, then the overall appearance of the output is not considerably vitiated by small inaccuracies in the coordinates of the input atoms. The reason for all these useful properties is the simple fact that the mechanism behind the production of peaks in the accumulation function involves a search

and integration of the entire information contained by the Patterson function.

However, it is unfortunate that a systematic three dimensional calculation of iterations of pMA($\vec{u}$) function appears to be very difficult and time consuming with the present generation of commonly available computers. As a result, one is forced to use these functions in a role auxiliary to that of the more common image seeking functions. However, looking back into the fifties, how many of us would have dared to undertake the kind of three dimensional Fouriers and full matrix least squares that we are doing these days?

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DISCUSSION

M. J. Buerger asked whether the procedure of "chopping" the Patterson function would not lead to losing the interatomic peaks which correspond to single interactions. S. Raman answered in the negative, and went on to say that the "chopping" level may be chosen as (P min - gP min) where g is a factor less than unity, and may be anywhere between 0.5 to 0.9. He also emphasized that even if some peaks do get lost, the iterative procedure of minimum accumulation recovers the missing peaks.

J. Karle, U.S. Naval Research Lab:

In order to extend the coefficients on taking the transform of a Fourier map, it is necessary to alter the map. Otherwise, assuming good accuracy, the transform of a Fourier map will generate the original coefficients from which it was computed. One means of alteration would involve the elimination of all negative areas. Another would be, as Dr. Raman suggests, the removal of all positive peaks, whose magnitudes are smaller than the minimum possible from chemical considerations, from the map before taking the transform.